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ABSTRACTS
from
TRANSACTIONS published in JAPANESE

(Pages refer to the Japanese originals of this volume unless otherwise noted.)

Separation and Identification of Fatty Acids. Part 7.

Preparation of Erucahydroxamic and Brassidohydroxamic Acids, and Isolation of Pure Erucic Acid.

(pp. 415～418)

By H. Yukawa and Y. Inouye.

(Biochemical Laboratory, Department of Agriculture, Kyoto Imperial University;
Received February 13, 1942.)

In previous papers of this series, the preparation methods of hydroxamic acid derivatives of fatty acids, following the recovering of free fatty acids as pure samples, have been published. In this present paper, the preparation of erucahydroxamic acid from erucic acid methylester and also from rape seed oil were described. And its melting point 75.5～76°C was determined, while that of free erucic acid is 34°C. It was proposed also, as in the cases of other acids, that the hydroxamic acid method would be serviceable in the preparation of pure erucic acid.

Brassidohyroxamic acid, which is an ethylene isomer of erucahydroxamic acid, was also prepared as silver cluster of needles, m.p. 97～98°C.

Studies on Ascorbic Acid. VIII.

The Relution between Ascorbic Acid and Vitamin A. (II).

(pp. 419～422)

By Kichinosuke Fujimura.

(Laboratory of Nutritional Chemistry, Dept. of Agriculture and Chemical Institute, Kyoto Imperial University;
Received January 23, 1942.)

Dietary studies on the Increase of Utilizing Value of Northern Farm Animalls.

V. Experiment on Fox with Hydrolyzed Products of Human Hair.

(pp. 423~426)

By E. Takahashi and K. Shirahama.

(Department of Agriculture, Hokkaido Imperial University;
Received January 6, 1942.)

On the Synthesis of Amino Acid-glycosides. Part 1.

Synthesis of Tyrosine-N-glycosides.

(pp. 427~432)

By Y. Inouye and K. Onodera.

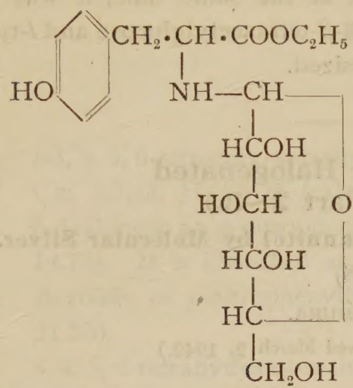
(Biochemical Laboratory, Department of Agriculture, Kyoto Imperial University;
Received February 13, 1942)

Although the presence of carbohydrates in proteins is well known, the manner of linkage of sugars as a constituent in protein molecules has been very little investigated. In the authors' laboratory, some glycosides were already isolated from proteins (unpublished), in which sugar and amino acid or peptide were combined together as glycoside and such linkage in proteins may be considered to occur widely in nature. In the present work, the authors undertook the serial synthesis of amino acid-glycosides, in two types i.e., N- and O-glycosides, for the purpose of the confirmation of chemical structure of isolated glycosides and the determination of biochemical natures of such glycosides.

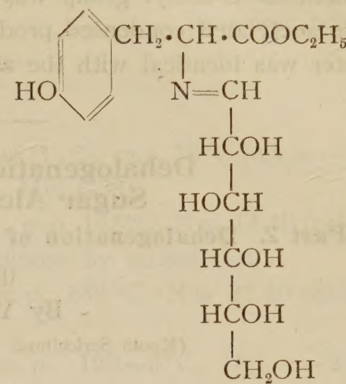
Tyrosine ethylester was condensed with sugar directly in absolute alcohol in the presence of trace of conc. HCl or glacial acetic acid. For instance, in 50 cc of abs. alcohol, 4.0 g of *l*-tyrosine ethylester and 3.2 g of glucose were suspended with one drop of glacial acetic acid and heated on the water-bath for about 80 min. At the end of this time, a clear solution was obtained and after evaporating in vacuum, the crystallization of the resulting syrup was attempted but hygroscopic powder was obtained. 3 g of the powder was acetylated in pyridine and after recrystallization, 2 g of pentaacetyl-tyrosine-ethylester-N-*d*-glucoside was obtained; melting pt. 140~141°, needles. By a similar process, N-*d*-mannoside, -*d*-galactoside, -*d*-fructoside, -*d*-arabinoside, -*l*-rhamnoside and -*d*-xyloside were prepared, but all of the glycosides except *d*-galactoside and *l*-rhamnoside were non-crystalline.

l-Tyrosinemethylester-N-*d*-glucoside, decomp. pt. 113°, needles; *l*-Tyrosine-methylester-N-*d*-glucoside + H_2O, decomp. pt. 110°, needles; *l*-Tyrosine-ethyl-ester-N-*d*-galactoside, decomp. pt. 118~120°, needles; *l*-Tyrosine-ethylester-N-*l*-rhamoside + H_2O m.p. 110~112°, needles.

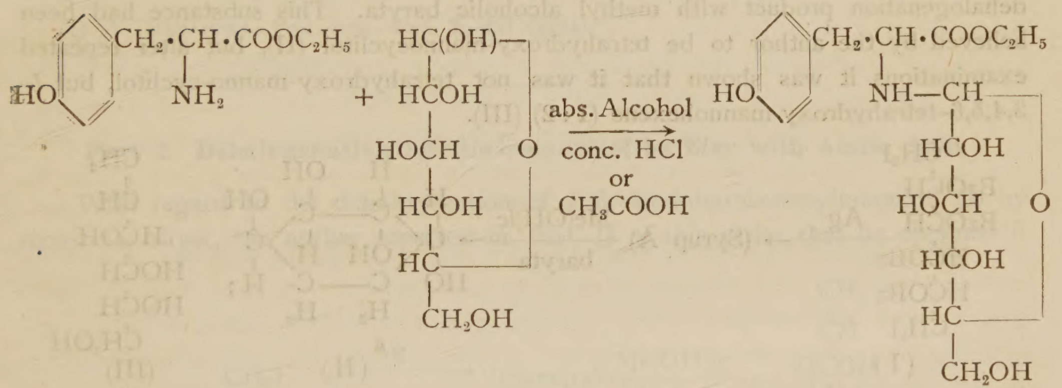
On the combination of amino group and carbonyl group of sugars, it may be possible to form either N-glycoside or Schiff's base; that is, sugar component remains in oxide ring form (I) or in open chain form (II)

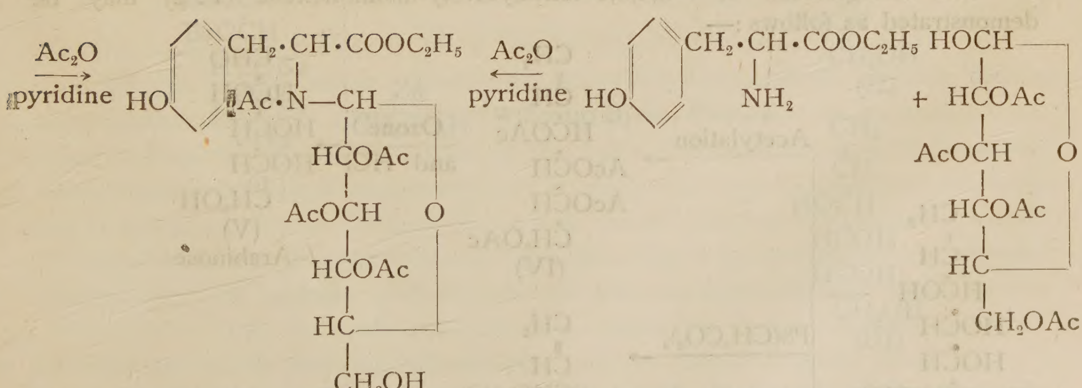


(I) N-glucoside
(α or β)



(II) Schiff's base
(*cis* or *trans*)





pentaacetyl-*l*-tyrosine-ethylester-N-*d*-glucoside

The authors confirmed their synthesized glycosides as N-glycosides by the fact that the determination of total acetyl radicles by Freudenberg's method indicates the presence of 5 acetyl groups in the molecule, while, by Kunz's method, the content of O-acetyl group was four. And at the same time, it was proved that the acetylated condensed product of 2,3,4,6-β-tetraacetylglucose and *l*-tyrosine-ethylester was identical with the above synthesized.

Dehalogenations of the Halogenated Sugar Alcohols. (Part 2~3.)

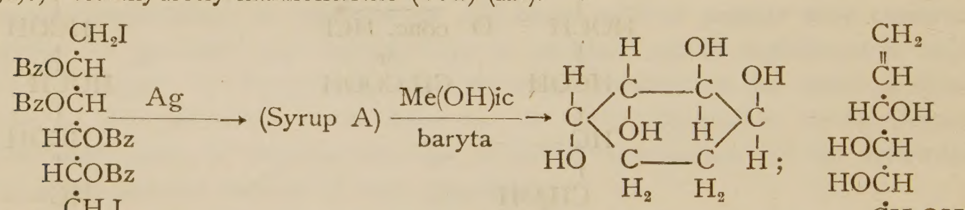
Part 2. Dehalogenation of 1,6-diiodomannitol by Molecular Silver.

(pp. 433~438)

By Yasuji HAMAMURA.

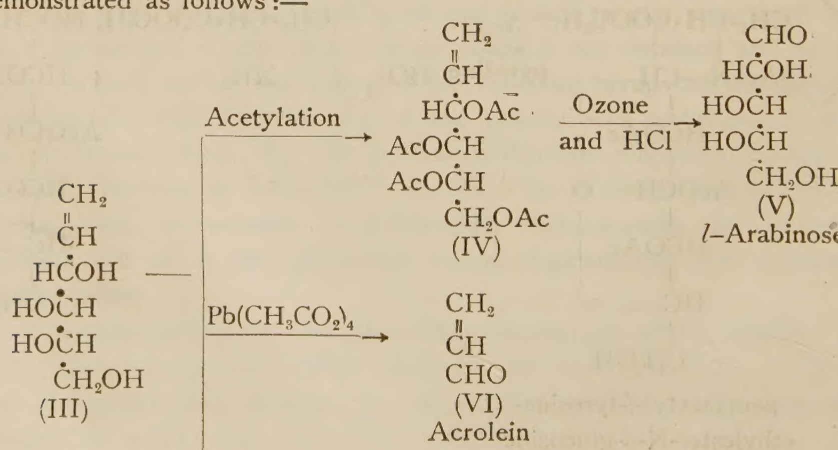
(Kpoto Sericultural college; Received March 2, 1942.)

The author once made an attempt to derive polyhydroxycyclohexane (II) from 1,6-diiodotetrabenzoyl-mannitol (I) by the action of molecular silver and succeeded in getting a crystal, m.p. 148°C., $[\alpha]_D = -27.00$, $C_6H_{12}O_4$, by hydrolysing the dehalogenation product with methyl alcoholic baryta. This substance had been believed by the author to be tetrahydroxy-mannocyclitol (II), but after repeated examinations it was shown that it was not tetrahydroxy-manno-cyclitol, but *l*-3,4,5,6-tetrahydroxy-mannohexene (1 : 2) (III).

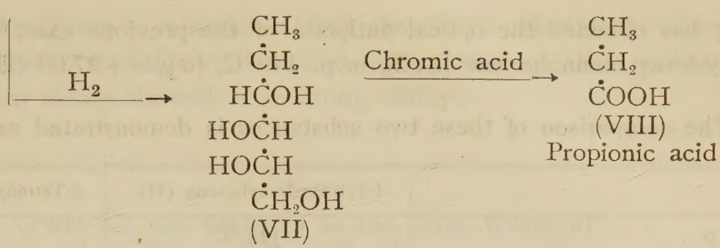


(I) (II) (III)

The configuration of *l*-3,4,5,6-tetrahydroxy-mannohexene (1 : 2) may be demonstrated as follows :—



(III) (IV) (V) *l*-Arabinose (VI) Acrolein



IV. l-3, 4, 5, 6-tetracetyl-tetrahydroxyhexene (1 : 2), m.p. 79°C, $[\alpha]_D = -59.00°$, C% 53.43, H% 6.25 (calc. C% 53.13, H% 6.38).

V. l-Arabinose as p-nitrophenylhydrazone, m.p. 183°C, N% 14.59 (calc. N% 14.73). It is identified as natural arabinose by mixed test.

VI. Acrolein as p-nitrophenylhydrazone, m.p. 158°C, N% 21.40 (calc. N% 21.95).

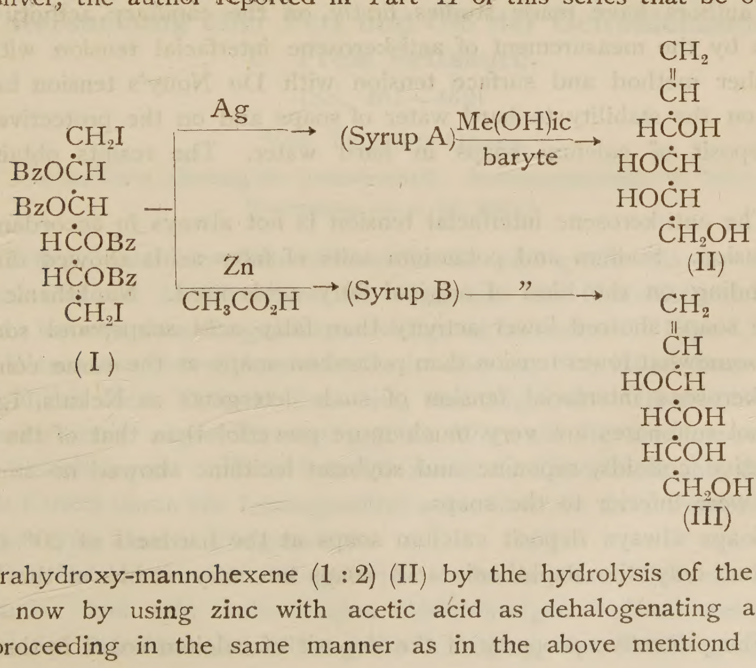
VII. 3, 4, 5, 6-tetrahydroxy-mannohexane, m. p. 123~5°C, $[\alpha]_D = -24.4$ (in borax solution). C% 47.68, H% 9.18 (calc. C% 48.00 H% 9.33).

VIII. Propionic acid as p-bromophenacyl ester, m.p. 61~62°C, C% 48.34, H% 3.95 (calc. C% 48.70, H% 4.08).

(1) Y. HAMAMURA: Proc. Imp. Aced. X, 459 (4934).

Part 3. Dehalogenation 1,6-diiodomannitol by Zinc with Acetic Acid.

With regard to the dehalogenation of 1, 6-diiodotetrabenzoylmannitol (I) by molecular silver, the author reported in Part II of this series that be obtained l-



3, 4, 5, 6-tetrahydroxy-mannohexene (1 : 2) (II) by the hydrolysis of the benzoyl-ester. But now by using zinc with acetic acid as dehalogenating agent and otherwise proceeding in the same manner as in the above mentiond case, the

author has obtained the optical antipode of the previous case, that is, *d*-3,4,5,6-tetrahydroxy-mannohexene (1 : 2), m.p. 148°C, $[\alpha]_D = +27.00$ (III)

The comparison of these two substances is demonstrated as follows :—

	l-Tetrahydroxyhexene (II)	*d*-Tetrahydroxyhexen (III)
m. p.	148.°C	148°C
$[\alpha]_D$	−27.00°C	+27.00°C
Acetylated, m. p.	79°C	79°C
,, $[\alpha]_D$	−59°	−58.02°C
Oxidation by ozone	*l*-arabinose	*d*-arabinose
,, by $Pb(CH_3CO_2)_4$	acrolein	acrolein

(1) Hamamura : J. Agr. Chem. Soc. Japan., 18, 433 (1942).

Chemical Studies on Agricultural Insecticides. (Part 1∼2.)

(pp. 439∼450)

(Part 1.) On the Capillary Activity and Stability to Hard Water of Emulsifiers.

By Chiyoka Mouri and Seiichi Izume.

(Central Laboratory, South Manchuria Railway Company, Dairen ;
Received February 9, 1942.)

The authors have made studies firstly on the capillary activity of various emulsifiers by the measurement of anti-kerosene interfacial tension with Hillyer's drop number method and surface tension with Du Nouy's tension balance, and secondly on the stability to hard water of soaps and on the protective properties of the deposit of calcium soaps in hard water. The results obtained are as follows :

1. The anti-kerosene interfacial tension is not always in accordance with the surface tension. Sodium and potassium salts of fatty acids showed different activity depending on the kind of original fatty acids used. Naphthenic acid soaps and resine soaps showed lower activity than fatty acid soaps, and sodium soaps showed a somewhat lower tension than potassium soaps at the same concentrations. The anti-kerosene interfacial tension of such detergents as Nekals, Igepons, and fatty alcohol sulfonates are very much more powerful than that of the soaps. Of the protective colloids, saponine and soybean lecithine showed no small activity, but these were inferior to the soaps.

2. Soaps always deposit calcium soaps at the hardness of 20° (by German degrees), but only the naphthenic acid soaps are very stable at the hardness of 70°.

3. The protective property of the deposit of calcium soaps in the hard water

of some of the detergents is remarkable, but showed no relationship with its stability to hard water. Protective colloids such as saponine, gelatine, sodium ligninsulfonate and gum arabic showed very strong ability.

(Part 2.) On Stability to the Hard Water of Kerosene-Soap Emulsions.

The authors have investigated the stability to hard water of kerosene-soap emulsions with the following results:

1. The relationships between the concentrations of kerosene in kerosene-soap emulsions and their dispersion conditions in hard water are studied in the test tubes. If the content of kerosene is low, solid deposits are formed; on the other hand, if the content is high, many oily deposits are formed. The most suitable concentration is 0.25%.

2. The stability to hard water of kerosene-soap emulsions of various kerosene contents is tested. Solid or oily deposits are formed at the hardness above 30°, but creamings are formed only at the hardness under 30°.

3. The effects of protective colloids added to the solutions of kerosene-soap emulsions in hard water are compared. While the addition of such materials as saponine, sodium ligninsulfonate and gum arabic is very effective in promoting the stability to hard water of the emulsions, gelatine has very little effect.

Untersuehung über Fett und Öle der Getreidefenniche I. Freie Fettsäure.

(SS. 451～462)

Von Tetsujiro OBARA.

(In der Chem Abteilung der Landwirtschaftl. Erziehungsfachschule zu Tokyo.
Eingegangen am 6. 12. 1941.)

Der Fettöl-Gehalt des Getreidefennichs ist viel größer als der der anderen Gramineae, und die Fettölmengen der Karyopse des Getreidefennichs betragen 5.0～6.5%; insbesondere die gereinigte Menge ist bedeutend. Eine Untersuchung über das Wesen des Getreidfennichfettöls ist aber im Schrifttum kaum zu finden. Ich habe, durch diese Tatsache veranlaßt, eine allgemeine Untersuchung über das Getreidefennichfettöl angestellt, den größten Wert auf die Zusammensetzung des neutralen Fettöls legend: daher habe ich zuerst ein Experiment über die Fraktionierung des Fettöls durch ein Lösungsmittel sowie über die freie Fettsäure angestellt und folgende vier Punkte klargemacht:

i) Das Getreidefennichfettöl gehört zum halbtrocknen Fett, die fraktionierte Teilung außer dem zum sechs eckigen blätterförmigen Kristall werdenden Teil, welcher in der Petroleum-Ätherlösung durch Lösung des Fettöls gesättigt wurde

und dem durch Aceton prezipitierenden Teil, wurde mittels Alkohol durchgeführt. In dieser Teilung, die mittels des 90% igen Alkohols ausgeführt ist, sammelt sich die freie Fettsäure, weiter werden von dieser Teilung die freie Fettsäure und das neutrale Fettöl getrennt.

Unter den Ausbeuten durch diese Experimente betrugen der unlösliche fraktionierte Teil mittels des 99%igen Alkohols etwa 50%, der mittels des 90%-igen Alkohols dagegen etwa 31%, der lösliche mittels des 90%igen Alkohols etwa 10% und der der freien Fettsäure beinahe 8%.

Dazu ist hier noch zu betonen, daß jede Teilung des neutralen Fettöls ihre eigene andersartige Eigenschaft habe.

ii) Die freie Fettsäure besteht aus etwa 11%iger fester Fettsäure und ungefähr 86%iger flüssiger Fettsäure.

iii) Die feste Fettsäure besteht meistens aus Palmitinsäure und enthält diejenige Säure, die für eine geringe Menge höherer Säure, d. h. für eine winzige Menge Arachinsäure gehalten wird.

iv) Die flüßige Fettsäure besteht aus 70%iger Ölsäure und 27%iger Linolsäure.

On the Manufacture of Artificial Fibres from Proteins. (Part II).

On the Artificial Fibres of Soy-bean Protein.

(pp. 463~466)

By Masami OKU and Yutaka HOSOKAWA.

(From the Chemical Fibre Laboratory, Ueda Imperial College of Sericulture and Silk Industry;
Received January 31, 1942.)

Studies on Digestion of Soy-beans (Benzine Extracted) as Rice Substitute.

(pp. 467~495)

By T. CHACHIN and M. KUBO.

(Osaka Municipal Hyg. Lab.; Received January 28, 1942.)

The authors recommended the soy-beans extracted with benzine as the rice substitute.

The digestion coefficients in rice or 10% soy-beans mixed are as follow:

	Protein %	Fat %	Carbohydrate %	Fibre %	Ash %	Calorie %
Rice	83.47	84.67	99.43	68.73	82.28	95.23
10% Soy-beans mixed	84.20	84.52	99.39	68.31	85.02	95.41
Rice	83.50	84.63	99.49	66.54	81.18	95.59

Studies on the Components of the Bark of Rhamnus japonica (VI).

The Chemical Structures of α-Sorinin and α-Sorigenin.

(pp. 496～502)

By Zirô NIKUNI.

(Agr. Chem. Laboratory, Tokyo Imp. Univ.; Received February 21, 1942.)

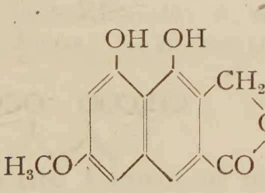
In the previous paper[1] it is reported that α-sorinin is the lactone of x-primverosido-x-methoxy-1 or 4-hydroxy-3-hydroxymethyl-2-naphthoic acid.

Kostanecki[2], Perkin[3] and others have found that it is very difficult to alkylate the hydroxyl group occupying the ortho-position relatively to the carbonyl or carboxyl group present in members of xanthone, flavone, anthraquinone, acetophenone and benzoic acid.

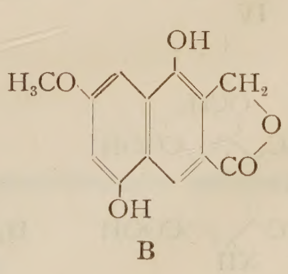
It thus appears that the free hydroxyl group of α-sorinin must be on 4 position of the naphthalene nucleus. Because this hydroxyl group is methylated very easily.

Then the oxidation of α-sorinin with potassium permanganate was tried. 2.0 g of the glycoside was dissolved in 100 cc dilute potassium hydroxide solution and drop by drop 140 cc of 3% potassium permanganat solution war added. The reaction mixture was acidified and extracted with ether. Faintly yellowish needles (m.p. 177～179°) were obtained from the extract by recrystallizations from toluene. Yield 41 mg. From the analytical results and absorptions spectrum, it was decided that this substance is either 5-methoxy-3-hydroxy-phthalic acid or 5-hydroxy-3-methoxy phthalic acid. On the other hand, this acid shows very intensitive reddish violet colour reaction with ferric chloride solution. So it must be 5-methoxy-3-hydroxy-phthalic acid[4].

To form 5-methoxy-3-hydroxy-phthalic acid by oxidation, α-sorigenin must have the structure of either A or B.



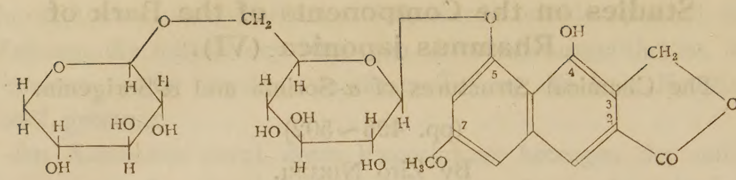
A



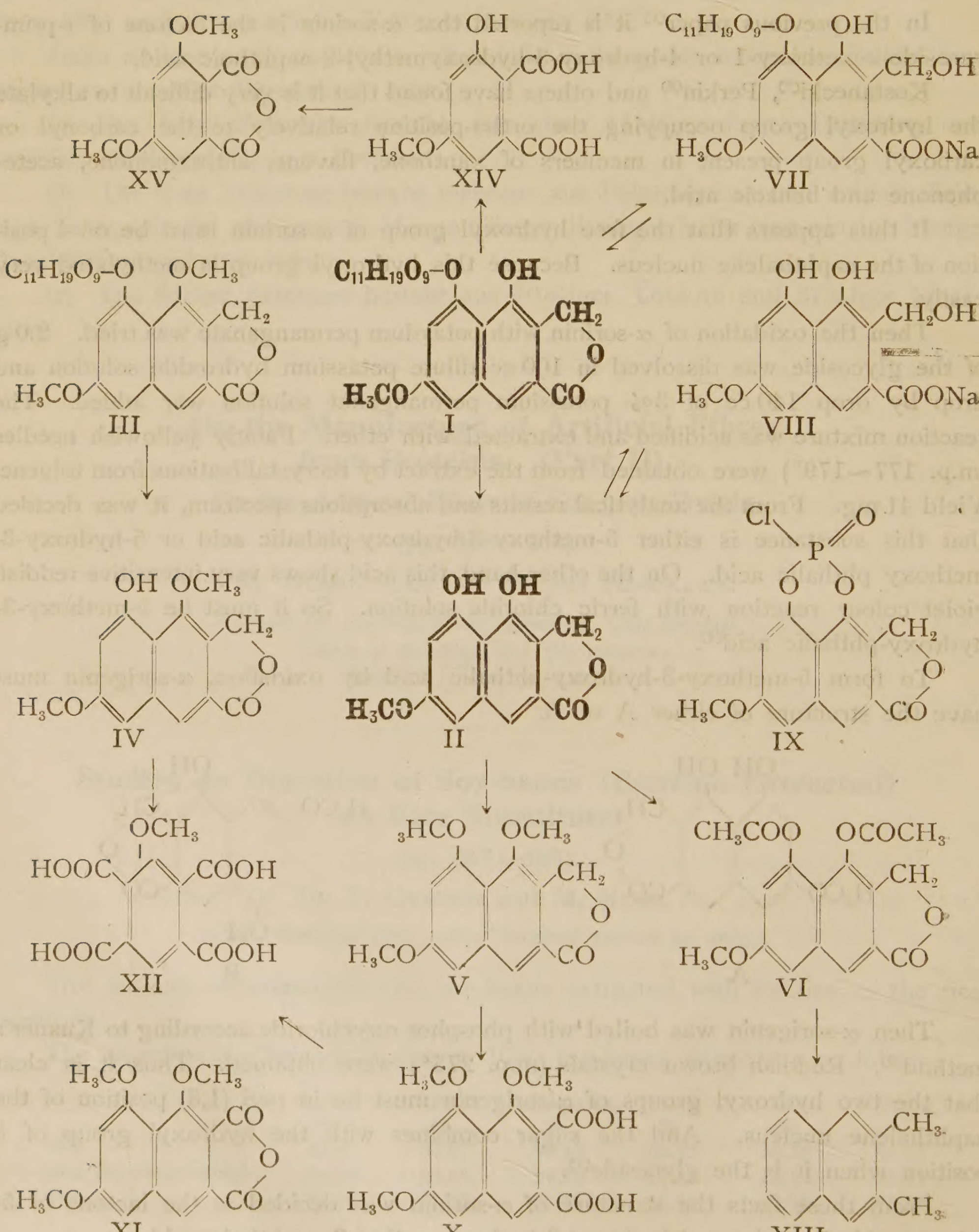
B

Then α-sorigenin was boiled with phosphor oxychloride according to Knauer's method[5]. Reddish brown crystals (m.p. 273°) were obtained. Thus it is clear that the two hydroxyl groups of α-sorigenin must be in peri (1,8) position of the naphthalene nucleus. And the sugar combines with the hydroxyl group of 5 position when it is the glyceside[1].

From these facts the structure of α-sorinin was decided as the lactone of 5-primverosido-7-methoxy-4-hydroxy-3-hydroxymethyl-2-naphthoic acid.



α-Sorinin



α-Sorinin and its derivatives are listed below. And the figures show the deriving process of these compounds. Among these compounds only 2,3-dimethylnaphthalene (XIII) and 3,5-dimethoxy-phthalic anhydride (XV) are known substances.

In conclusion the author desires to express his sincere thanks to Prof. Bunsuke Suzuki for his kind guidance throughout this work, and to the Imperial Academy for a grant, which has in part defrayed the cost of this investigation.

(I)	α-Sorinin	m.p. 159°
(II)	α-Sorigenin	227～229°
(III)	Methyl-α-sorinin	242～243°
(IV)	Monomethyl-α-sorigenin	197°
(V)	Dimethyl-α-sorigenin	183.5～184.5°
(VI)	Diacetyl-α-sorigenin	259°
(VII)	α-Sorinic acid Na-salt	260～270° (blackend)
(VIII)	α-Sorigenic acid K-salt	above 280°
(IX)	α-Sorigenin-oxychlorphosphine	273°
(X)	4,5,7-Trimethoxynaphthalene-2,3-dicarboxylic acid	263°
(XI)	Anhydride of 4,5,7-Trimethoxynaphthalene-2,3-dicarboxylic acid	263～264°
(XII)	Monomethoxy-pyromellithic acid	251°
(VIII)	2,3-Dimethylnaphthalene	90～96°
(XIV)	5-Methoxy-3-hydroxy-phthalic acid	177～179°
(XV)	3,5-Dimethoxy-phthalic anhydride	151～152°

Literature.

(1) Nikuni: Bull. Agr. Chem. Soc. of Japan, **17**, 92 (1941).
(2) Dreher, Kostanecki: B., **26**, 71 (1893).
(3) Perkin: Soc., **71**, 812 (1897).
(4) Asahina, Hayashi: B., **66**, 1023 (1933).
(5) Knauer: B., **27**, 2565 (1894).

On the Tannin of the Leaves of *Lagerstroemia subcostata*.

(pp. 503～506)

By Minoru Ishii.

(Agricultural Chemical Institute, Taihoku Imperial University;
Received February 12, 1942.)

From the leaves of *Lagerstroemia subcostata* Kochne, which contain about 15% tannin in the dry matter, pure tannin and ellagic acid were isolated by the author. The tannin showed dextro rotation and could be decomposed neither by Aspergillus niger nor by emulsin. It was confirmed to be a diglucoside of luteoic acid by acid hydrolysis, which yielded ellagic acid and glucose in the molecular ratio

of 1 and 2. On the other hand, alkali hydrolysis of the methylated tannin gave tetramethoxy luteoic acid.

Untersuchungen über die Beziehungen von Bataten zur Alkoholproduktion. (III).

(SS. 507～520)

Von K. Suematu und M. Utikosi.

(The Institute of Reserch on Chemical Industry, Government-General of Taiwan, Japan; Received January 6, 1942.)
